INFRARED SPECTROSCOPIC STUDIES; THE EFFECT OF ACIDS AND BASES ON THE INFRARED SPECTRUM OF LIQUID WATER

BY
JESSE BERNARD PATBERG
A.B., Evansville College, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

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INFRARED SPECTROSCOPIC STUDIES; THE EFFECT OF ACIDS AND BASES ON THE INFRARED SPECTRUM OF WATER

Introduction

The water problem, its anomalous colligative properties and its role in animal and plant life, has been of great interest to the scientist for a number of years. The methods employed in the study of this problem have been many and varied[1, 2] and some of the early explanations suffered greatly from a lack of an understanding of the mechanism of the bonding of the water to animal and plant tissue and a knowledge of the structure of liquid water.

Correlation of the hydrogen bond hypothesis of Latimer and Rodebush[3] with the spectroscopic work of Coblentz[4] led Buswell[5] to postulate that the water is bonded through the hydrogen bond. Later Wulf and Liddel[6] showed spectroscopically that the first harmonic of the OH group "disappears" when hydrogen bonding is possible. This observation established infrared spectroscopy as the most direct and the most practical method of studying the water problem.

In this study the infrared technic has been used exclusively to observe the shifts of the absorption bands of liquid water upon the introduction of polar solutes. A review of the work done on problems related to this subject is included in the thesis.

Experimental

The spectrometer used is the prism type of instrument built in this laboratory in 1936.[7] The prism is made of rock salt and is a 60° prism 8 centimeters high and 10 centimeters on a side. The thermocouple is of the compensating type and feeds a simple photoelectric amplifier. The source is a coiled tungsten filament operated at 4 to 6.5 amperes at about 6 volts in an atmosphere of argon. The radiation leaves the source through a cleaved rock salt window.

The aqueous solutions studied were made up to known concentrations by dissolving weighed amounts of reagent grade material in distilled water and diluting to known volume. For those solutes which were already available as solutions dilutions were made and the concentration determined by titration methods. The densities of these solutions were determined by means of the Westphal balance.

The spectra of the aqueous solutions were determined by running films of known thickness against the same thickness of pure liquid water. This technic cancelled out the normal water spectrum, and only the changes in the water spectrum effected by the dissolved substance were observed. However, since in most cases both sides of the cell did not contain the same number of water molecules as the solution, some being displaced by the solute molecules, a correction was necessary. Since it was found that the extinction coefficient of water varies with the thickness of the water film, it became necessary to determine the spectra of several thicknesses of water in order to establish this correction.[8]

Solutions of LiOH, NaOH, KOH, HCl, HBr, HI, H_2SO_4 and H_3PO_4 ranging in concentration from 1.25 molar to their saturated solutions were studied. The greater part of this work has been done in the region about the 1.96 and 1.44 mu bands of water. These bands have been shown previously[9] to undergo significant changes as the physical environment of the water is changed.

Results

Spectra for various acids and bases were obtained using various concentrations and thicknesses. The extent of the shift of five bands of liquid water, those at 6.1, 4.7, 2.96, 1.96, and 1.44 mu was observed. These spectra were corrected for water content, and the extinction values of the solutions plotted against the wave length.

The adjoining table illustrates the fact that for the three general classes of solutes studied, alkalies, halogen acids and oxy-acids, the extent of the shift is approximately the same for the same molar concentration. The data listed pertain to

1.25 molar solutions of the three classes of solutes.

Water Bands	Aqueous Solution of NaOH	HCl	H_3PO_4
6.1 mu	5.35	5.32	
4.7	4.40	4.40	
2.96	3.65	3.65	3.64 mu
1.96	2.25	2.25	2.28
1.44	1.89	1.86	1.88

The direction and the extent of the shift depends upon the type of vibration giving rise to the absorption. For instance, bands involving a valency vibration are shifted to lower frequencies while those involving bending vibrations are shifted to higher frequencies. For the lower concentrations the shifted bands appear at 5.35, 4.4, 3.65, 2.24 and 1.85 mu.

Data showing the change of the extinction values with concentration for the peaks at 2.24 and 1.85 mu were carefully taken, and the extinction values were plotted against the molar concentration of the particular solute. This plot indicated that the height of the peak was not a linear function of the concentration.

Discussion

Some degree of explanation for these band shifts can be reached by a consideration of the water molecule and the structure of water in the liquid state. It has been previously shown that all of these bands experience similar shifts when water undergoes a change of state[10] and a consequent change of molecular structure. As the molecules of water move more closely together the hydrogen bonds become stronger and the bonds between the hydrogens and the "mother" oxygen become proportionately weaker. Under these conditions it is expected and observed that the frequency of the bending vibration be increased and that of the valency vibration be decreased.

The same sort of effect is to be expected when a charged body is brought into position so that bonding is possible between ion and water molecules. Bonding to form the hydrated

hydrogen ion or the hydrated hydroxyl ion would then cause a weakening of the normal bonds of the water molecule with the corresponding change in the frequencies of the vibrations of the hydrogens. The ion of an oxy-acid would be expected to have a similar effect.

The concept that these new bands which thus appear are simply the original liquid water bands, which have been shifted according to the mechanism described above, is supported by the analysis of the spectra obtained. Assuming that the bands which appear at 5.35 and 3.65 mu are due to the normal bending vibration and unsymmetrical valency vibration respectively, we can calculate the position at which the various combination bands would appear. When it was found that these calculated frequencies agreed very well with the observed frequencies the assumption was considered to be upheld, and the concept of shifted water bands verified.

The curves obtained by plotting extinction values versus concentration of solute show a definite change of slope in the higher concentrations. This would seem to indicate that with increasing concentration there is a point at which all association positions for the ions are filled and the effect is no longer dependent upon changes of concentration.

The curves obtained in this manner for H_3PO_4, which gives higher extinction values than the same molar concentration of the halogen acids, seem to indicate that the undissociated acid molecule also plays its role in the effect on the valency bonds of the water molecule, especially if the acid is an oxy-acid with its available donor atoms. The data for the halogen acids refute the idea that the undissociated molecule is the sole cause of the effect.

Another significant fact is the apparent change of slope of these curves in the very concentrated solutions, for example 12 molar H_2SO_4. It seems logical that the molecules of sulfuric acid, when present in concentration sufficient to give an appreciable degree of association, would show absorption in these regions. Thus, after the bonding positions of the water molecules are completely filled, any additional acid molecules are

free to bond to each other, giving rise to their characteristic absorption.

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VITA

Jesse Bernard Patberg was born in Huntingburg, Indiana on January 9, 1917, completing grammar and high school there during the years 1923 to 1934. He held a scholarship to Evansville College, Evansville, Indiana for four years and received his A. B. degree in June, 1938. In September, 1938 he began graduate work at the University of Illinois. While there he held a teaching assistantship for one year and a Special Research Assistantship in physical chemistry for the remaining two and a half years. He is a member of Sigma Xi. With Dr. R. C. Gore he is the co-author of a recent publication; Ind. Eng. Chem., Anal. Ed., *13*, 768 (1941).